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AUTHOR(S):

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Fluorous Property of a Short Perfluoroalkyl-Containing Compound Realized by Self-Assembled Monolayer Technique on a Silicon Substrate

Ryuma Kise¹, Aki Fukumi¹, Nobutaka Shioya¹, Takafumi Shimoaka¹, Masashi Sonoyama², Hideki Amii², Toshiyuki Takagi³, Toshiyuki Kanamori³, Kazuo Eda⁴ and Takeshi Hasegawa^{1*}

¹Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

²Division of Molecular Science, Faculty of Science and Technology, Gunma University, Kiryu, Gunma 376-8515, Japan

³National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

⁴Department of Chemistry, Graduate School of Science, Kobe University, 1-1 Rokko-dai, Nada-ku, Kobe, Hyogo 657-8501, Japan

E-mail: htakeshi@scl.kyoto-u.ac.jp



Takeshi Hasegawa

Takeshi Hasegawa received PhD from Kyoto University. He was appointed to be Assistant Professor at Kobe Pharmaceutical University in 1993 and Lecturer in 2001. After he experienced Associate Professor at CIT, Nihon University (2003), Researcher of JST PRESTO (2004), and Associate Professor at Tokyo Institute of Technology (2006), he joined ICR, Kyoto University as Full Professor in 2011. He is a Fellow of Society for Applied Spectroscopy (USA) after recognition of his original spectroscopic technique of “pMAIRS.” The SDA theory is another his exciting topic.

Abstract

Fluorous properties represented by the water-and-oil repellency are perfluoroalkyl (R_f) compounds-specific characters, which are widely used for surface coating of glass, an electronic device and textiles for preventing water and greasy fouling. According to the stratified dipole-arrays (SDA) theory, the minimum R_f length of $(CF_2)_7$ is theoretically necessary for realizing the fluorous property. Unfortunately, however, compounds involving this chemical unit are strictly banned for fabrication because of a concern of environmental pollution, which is a big dilemma. Here, we show that the fluorous property can be realized by the self-assembled monolayer (SAM) technique even with a short R_f -containing compound, since the SAM technique makes the best use of the self-aggregation property of the R_f groups, and it readily makes the molecules immobile.

Keywords: Short perfluoroalkyl-containing compound, Self-assembled monolayer technique, Fluorous surface property

1. Introduction

Perfluoroalkyl (R_f) compounds are characterized by the unique “fluorous” properties represented by the water-and-oil repellency, which cannot be realized by non-fluorine compounds.¹ The fluorous property is strongly correlated with the molecular interaction between the R_f chains.² For many years, this has often been discussed on London’s dispersion force, as commonly found in normal hydrocarbon compounds, which is, unfortunately, an obstacle for comprehensive understanding of the material properties of R_f compounds.^{2,3}

To discuss the molecular interaction of R_f groups in a physicochemical manner, we have to pay attention that each C–F bond has a large permanent dipole moment due to the large electronegativity of fluorine³, and in addition, an R_f group has a helical conformation about the molecular axis.^{4,5} As a result, the R_f groups having the length of $(CF_2)_7$ or longer are spontaneously aggregated to yield “two-dimensional dipole-arrays with various directions,” which is a dipole-array network. This spontaneous aggregation mechanism is known to be the

stratified dipole-arrays (SDA) theory.^{2,6} The comprehensive understanding of the fluorous properties fundamentally requires the SDA theory; whereas the hydrophobicity is partly attributed to the surface morphology.⁷

On the SDA theory, the R_f length of $(CF_2)_7$ is the critical minimal length for inducing the ‘spontaneous’ aggregation, and the fluorous property is, in fact, induced by the molecular aggregate of $(CF_2)_7$ or longer.^{1,2,6} This boundary length is often found in various compounds, and poly(fluoroacrylate) (PFA) is one of the good examples. PFA has side chains, each of which has an R_f substitute. If the substitute is the perfluorooctyl group (i.e., $-(CF_2)_7CF_3$) or longer, PFA exhibits an apparent fluorous property; whereas the property is lost for a shorter R_f substitute.⁸ This critical length of $(CF_2)_7$ works as a key not only for a useful material function, but also for a troubling property.

PFOX represented by perfluorooctyl sulfonate (PFOS) and perfluorooctanoic acid (PFOA) has recently been pointed out to be troubling: they are toxic and persist in environment for a long-term period.⁹ The same problem is true of a longer R_f compound. The critical chemical group is the perfluorooctyl group that involves the unit of $(CF_2)_7$. On the SDA theory, these compounds would spontaneously make a molecular aggregate, and the tightly packed aggregate should be inappropriate for smooth metabolism, once they are uptaken into a human body. Therefore, PFOX or longer relatives are banned to be manufactured on considering the environmental pollution; whereas the critical length of $(CF_2)_7$ is necessary for realizing the useful fluorous properties,⁸ which is a big dilemma. A new technical recipe based on a comprehensive theory is therefore strongly needed for realizing the fluorous property using a short R_f -containing compound having $(CF_2)_6$ or shorter.

Fortunately, we have an opportunity to reconsider a point of the SDA theory that the molecules are “spontaneously” aggregated for the length of $(CF_2)_7$ or longer. If we could “artificially arrange” short R_f groups closely in a two-dimensional (2D) manner, the surface property of the membrane is expected to be close to that obtained by PFOX.³

In the present study, a silicon (Si) substrate is chosen as the substrate, and artificially arranged molecular aggregates are prepared by using the Langmuir-Blodgett (LB)¹⁰ and self-assembled monolayer (SAM) techniques.^{11–18} Since a SAM

coverage is attained by controlling the surface reactivity with the substrate surface, SAM is an artificial molecular aggregate. As a result, very low surface energy is readily realized even for a short- R_f containing compound by the SAM technique; whereas the LB technique is inadequate for the stability of the hydrophobicity. In addition, the SAM technique is found to retain a very low surface energy for a long time without using PFOX.

2. Experimental

Chemicals. 1H, 1H, 2H, 2H-Perfluorododecyltrichlorosilane (FDDTS; R_f9) (97%) and 1H,1H,2H,2H-perfluorooctyltrichlorosilane (FOTS; R_f5), (97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTs; R_f7) (>96.0%) was purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Henicosafuorotetradecanoic acid (My- R_f9) for the discussion of the LB technique was synthesized as reported in our previous paper.⁶

The Si substrate was purchased from Valqua FFT Inc. (Tokyo, Japan) and cleaned in a conventional manner: sonication in pure water, ethanol, acetone, and dichloroethane for about 1 min each. All the organic solvents were guaranteed reagents. The substrate was oxidized using a Bio Force (Ames, IA) PC440 UV/ozone ProCleaner™ Plus for 10 min.

Langmuir-Blodgett (LB) Film. A Langmuir (L) film was prepared on pure water by spreading a solution of My- R_f9 , which was dissolved in a mixed solvent of methanol and chloroform (1 : 10 (v/v)), and the L film of a single monolayer was transferred onto a Si substrate by using the LB technique with a transfer ratio of 1.02. To prepare the LB film of CdMy- R_f9 , a buffered aqueous solution of cadmium chloride (CdCl_2) (1.0×10^{-2} M) was used as the subphase, in which sodium hydrogen carbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) were added to keep pH ≈ 7.5 .¹⁹ CdCl_2 was purchased from Rare Metallic Co. Ltd. (Tokyo, Japan), and the other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

The LB films were prepared by using a Biolin Scientific (Espoo, Finland) KSV-NIMA Minitrough Langmuir-Blodgett system. Pure water for subphase was obtained by a Millipore (Molsheim, France) Elix UV-3 pure-water generator and Symplicity UV System water purifier. The water exhibited an electric resistivity higher than 18.2 M Ω cm.

SAM Preparation. SAM reagents were dissolved in a fluorine containing solvent, HCFC-225 (1.0 mM), purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and a Si substrate was dipped in the solution for 60 min. To promote the SAM formation, the solution was kept at 70°C. Unreacted molecules remained on the SAM were washed away by ASAHIKLIN AK-225AES, made by Asahi Glass Co., Ltd. (Tokyo, Japan), and the solvent remained was removed in a dry oven at 60°C.

Contact Angle Measurements. Contact angle was measured using a Kyowa Interface Science Co., Ltd. (Saitama, Japan) DropMaster, DM-501Hy, contact-angle meter, with which the surface tension of pure water (72.5 mN m⁻¹) at 25 °C was checked. The drop of water (or diiodomethane (CH_2I_2) purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan)) with a volume of 2.0 μL was put on the sample surface, and the static contact angle was estimated. Time-dependent contact angle was measured every one second.

Grazing Incidence X-ray Diffraction (GIXD) Measurements. GIXD measurements were carried out on a high-resolution X-ray diffractometer (Rigaku SuperLab) equipped with a parabolic graded multilayer mirror. The X-ray was generated by using a Cu rotating anode generator (Cu $K\alpha$) operated at 40 kV and 30

mA. The scattered X-ray was collected by a scintillation counter. The diffraction pattern was measured with an in-plane geometry, with which the angle of incidence was fixed at 0.2°. The scan speed was 0.2° min⁻¹ and the sampling step was 0.03°.

3. Results and Discussion

LB-Film Approach. The LB technique is employed for preparing artificially aggregated molecules as a monolayer on a silicon substrate. An LB film of My- R_f9 prepared at a surface pressure (π) in the solid-film region (35 mN m⁻¹; Figure S1) was, however, very unstable and it was soon removed simply by putting a water droplet on the monolayer for a contact angle measurement as found in Figure 1a. In fact, the contact angle of this sample is the same as that on a bare surface of Si, which straightforwardly implies the removal of the LB film. The removal was confirmed by measurement of an IR spectrum (data not shown).

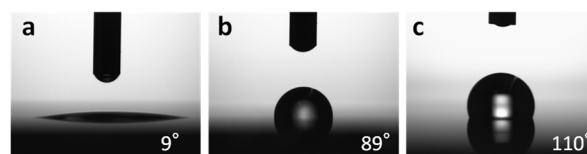


Figure 1. Contact-angle using a probe of a water droplet on (a) LB film of My- R_f9 , (b) LB film of CdMy- R_f9 and (c) SAM- R_f9 , each of which is prepared on Si.

The unstableness of the monolayer on the contact with a water droplet should be attributed to the hydrophilic property of the carboxylic group. In short, the monolayer was soon dissolved in water.

To avoid the hydrophilicity, a robust LB film was prepared from a monolayer ($\pi = 35$ mN m⁻¹) on a cadmium chloride aqueous solution with a concentration of 1.0×10^{-2} M at pH 7.5¹⁹ to make the monolayer a cadmium (Cd) “salt” of My- R_f9 (denoted as CdMy- R_f9). The π - A isotherm of the monolayer at 25°C is available in Figure S1. Since the Coulomb interaction between the carboxylate anion and Cd^{2+} is strong, the monolayer of the Cd salt is known to be stiff.¹⁹ In this manner, a highly packed molecular aggregate is obtained with an aid of both monolayer compression and chemical aggregation by Cd^{2+} . As expected, this LB film was not removed by the water-droplet probe.

Contrary to our expectation, however, the contact angle of the LB film of CdMy- R_f9 is 89° as shown in Figure 1a, which is apparently less than that of the reference data (ca. 119°) of a thick layer (100 nm) of $\text{C}_{20}\text{F}_{42}$.²⁰ Then, the same LB film is analyzed by GIXD measurements (Figure 2a). The GIXD patterns show a single peak at about $2\theta = 17.7^\circ$ reflecting a hexagonal crystalline packing,^{21,22} and its interplanar spacing ($d = 0.4996$ nm) is apparently larger than that of the reference data, i.e., 0.4936 nm of $\text{C}_{20}\text{F}_{42}$ calculated from the crystal data.²¹ This indicates that the molecular packing is not good enough even at the high surface pressure of 35 mN m⁻¹.

The correlation between the molecular packing and the surface pressure is presented in Figure 2a~d. The molecular packing is, as expected, systematically becoming looser on a decrease of the surface pressure. These changes are directly reflected by the contact angle as presented in Figure 2: the surface pressures of 35, 25, 15 and 5 mN m⁻¹ correspond to the contact angles of 89°, 78°, 64° and 42°, respectively, in a decreasing manner. This good correlation is understandable on the SDA theory. These results, therefore, imply that the molecular aggregation is a key for aiming at a high hydrophobicity using a short R_f compound.

The time-duration of the contact angle is of another interest. Figure 3 presents time courses of the contact angle measured on different two surfaces. The curve of the LB film of CdMy-R_f9 is shown in Figure 3a. This curve is impressive that the hydrophobicity is quickly lost especially in the very early stage within 30 sec. When compared to the criteria line of 119° (dashed line), the instability of the LB film is very apparent.

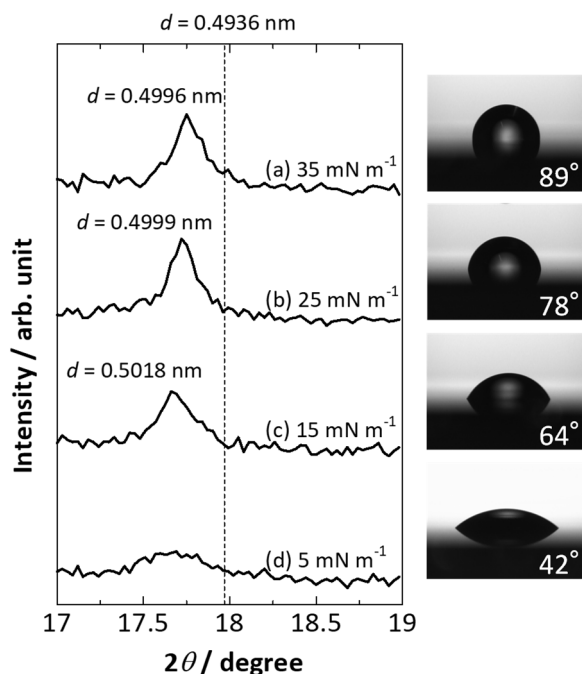


Figure 2. XRD (GIXD-IP) patterns of (a) a PTFE tape, and (b) an LB film of CdMy-R_f9 deposited at 35, (c) 25, (d) 15 and (e) 5 mN m⁻¹ on a Si wafer.

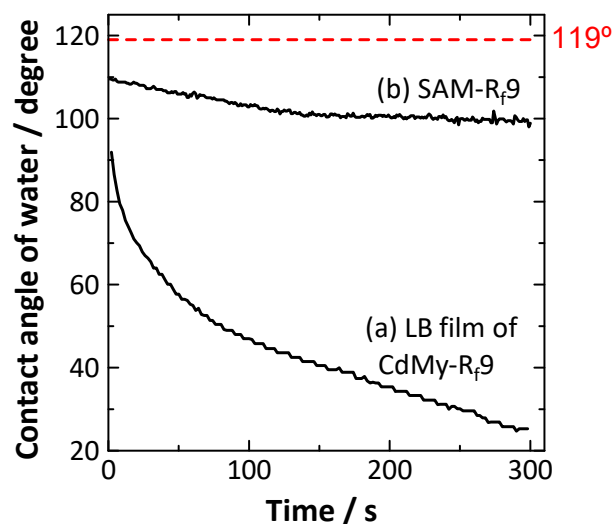


Figure 3. The time-courses of the contact angle measured on (a) the LB film of CdMy-R_f9, and (b) SAM-R_f9.

My-R_f9 is indeed stabilized by Cd²⁺ to be CdMy-R_f9, which works well for protecting the head group from the hydration when a water droplet is put on the LB film. Nevertheless, the contact of the head group with the substrate surface is made weaker by losing the hydroxyl group ((R-COO)₂Cd),¹⁹ since the metal salt cannot actively be interacted with the oxide surface via the hydrogen bonding. This weak interaction between the LB

film and the substrate should be an unstable factor of the ‘molecular mobility’ especially after putting a water droplet on it.

In this manner, for both cases of acid and salt, the LB technique is found *not* suitable for having a durable hydrophobic coating on a solid surface for a long time. In addition, the LB technique is not good for molecular packing, either, as discussed on Figure 2. As a conclusion, the best use of “spontaneous molecular aggregation” is necessary for a high hydrophobicity, and in addition the molecules should be immobile for a stable duration.

SAM Approach. To satisfy these two points simultaneously, the SAM technique is employed. Making a highly condensed and stable SAM on a Si surface is a little bit difficult task for normal hydrocarbons.¹²⁻¹⁷ The SAM formation requires nucleation of molecules at the initial stage, and the nucleus is developed by connecting with each other two-dimensionally.¹⁶ Very fortunately, R_f groups intrinsically have a nucleation property due to the SDA packing, which is quite suitable for the SAM formation.² In fact, the SAM of a silane-coupling reagent having an R_f group (FDDTS) was readily prepared in only 10 min. Both IR spectrum and GIXD-IP pattern (Figure S2) of the SAM apparently indicate that the SAM is ideally prepared in terms of molecular density and packing. In fact, as a result, the contact angle of the surface was 110° as found in Figure 1c. In addition, the time-duration is largely improved as found in Figure 3b: the decrease of the contact angle is stopped at about 100° that is good enough for the hydrophobicity.

In this manner, the SAM technique has proved to work for obtaining a highly durable hydrophobicity. To discuss the fluororous property, the surface free energy of SAM-R_f9 was measured by employing the add-and-remove volume method, and a very small value of 11.1 mJ m⁻² was obtained as found in Table 1.²³ As a reference, relevant results of SAM of octadecyltrimethoxysilane (SAM-ODS; normal alkyl) are also presented in the table, which are also results of the present study. The value of 11.1 mJ m⁻² is apparently smaller than the hydrocarbon (24.7 mJ m⁻²), which indicates that the surface of SAM-R_f9 is fluororous. Even if this value is compared to the top record (6.7 mJ m⁻²) on a bulk material (C₂₀F₄₂ with thickness of 100 nm) by Nishino et al.,²⁰ the free energy on the SAM can reasonably be recognized to be fluororous. Since the present result of a monolayer is comparable to the thick film, the SAM technique is found powerful for making the surface fluororous.

Table 1. Surface free energy of SAM-R_f*n* determined by the Owens method

	CA / °		Surf. Free Energy / mJ m ⁻²		
	Water	CH ₂ I ₂	γ _s ^d	γ _s ^p	γ
SAM-R _f 5	106.7	88.8	12.0	1.9	13.9
SAM-R _f 7	108.9	90.0	11.7	1.5	13.2
SAM-R _f 9	112.4	94.6	9.9	1.2	11.1
C ₂₀ F ₄₂ ²⁰	119	107	5.5	1.2	6.7
SAM-ODS	107.0	67.0	24.6	0.1	24.7

The dispersion and the polar components of the surface free energy (γ_s^d and γ_s^p, respectively) are both obtained by the Owens method using water and CH₂I₂ droplets (Table 1). Since the compound of SAM-R_f*n* has a primary structure of CF₃(CF₂)_n(CH₂)₂SiCl₃, the relative portion of the normal hydrocarbon part, i.e., (CH₂)₂, increases on a decrease of *n*, which induces the contribution of the “dispersion” part.^{2,3} In fact, γ_s^d increases from 9.9 to 12.0 mJ m⁻² systematically. At the same time, γ_s^p also increases slightly, which is because the summation of the dipoles of a short single R_f group cannot be close to zero, and even a collection of the molecules would not be close to zero,

either.^{2,3}

As expected on the SDA theory, a surprisingly low surface energy is obtained for the short compound. This means that the fluororous property can be realized even with a short- R_f chain containing compound by employing the SAM technique, which readily overcomes the “dilemma.”

The time-duration is also found excellent for the short- R_f compounds. The time-dependent static contact angles are presented in Figure 4. As found in this figure, the degradation is not significant especially for R_f7 . The contact angle of R_f5 is still decreasing with time, which should be correlated with the decrease of the receding contact angle of the dynamic measurements (data not shown).

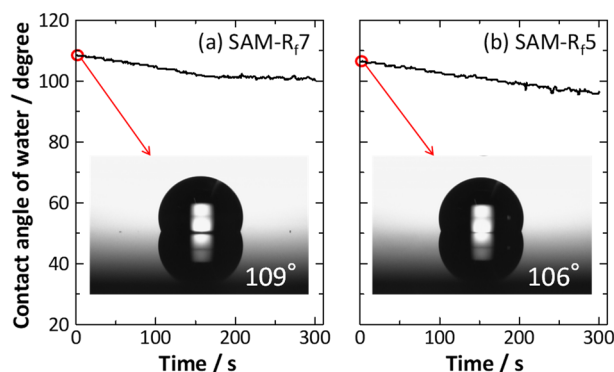


Figure 4. Time-dependent static contact angle on (a) SAM- R_f7 and (b) - R_f5 on Si at ambient temperature (ca. 25°C).

Here, we note that these results are much better than the contact angle of PFA. As typically reported by Takahara and co-workers,⁸ an R_f -containing polymer also obeys the SDA theory, and R_f5 is too short to exhibit a fluororous property. In this sense, the present results using the SAM technique is remarkable.

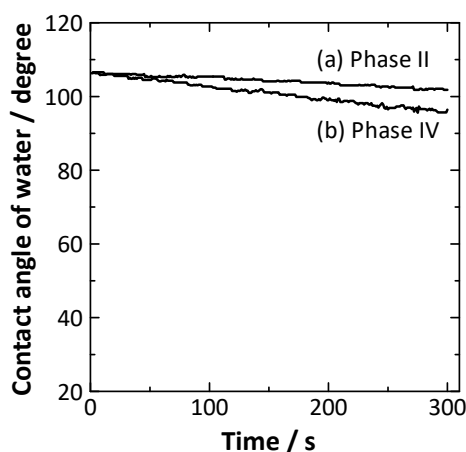


Figure 5. Time-dependent contact angle on the R_f5 -containing SAM measured at (a) 15°C and (b) 25°C.

In addition, we have to pay another attention to the phase transition (Phase IV to II) at 19°C. Above this temperature, the helical pitch about the R_f chain is a little bit loosen²⁴⁻²⁷ from the point group of D_{13} to that of D_{15} .^{27,28} As a result, temperature above 19°C is inappropriate for the molecular spontaneous aggregation, which is not good for exhibiting a fluororous property. In fact, the fluororous property of the R_f5 -containing PFA is drastically lost and the contact angle is less than 50° at a temperature above 19°C (cf. Fig. 11 in the reference #8).

On the R_f5 -containing SAM, in our present study, the contact angle at 15°C keeps a high value (Figure 5a), and the angle at

25°C still exhibits a larger value than 90° (Figure 5b), which can be recognized as hydrophobic.

In this manner, by employing the SAM technique, the silicon surface has readily been made fluororous using a short- R_f containing compound. On this concept, the conventional PFA technique proves to be also good, since the polymer main chain works as the substrate to make the side chains immobile, and the side chains are spontaneously aggregated. Regardless, the PFA technique relies only on the “spontaneous” aggregation, the length of R_f7 is critically necessary, for which the SAM technique should be better.

4. Conclusion

To make the solid surface fluororous, two points must be satisfied: 1) the molecules are immobilized on the surface, and 2) the best use of the spontaneous aggregation property of R_f groups should be made. In the present study, the SAM technique is found great for fulfilling the two points, on which the PFOX dilemma has readily been overcome.

To furnish a wide variety of material surfaces such as a textile on this concept, a tough coating technique of SAM being robust to repeat washing and UV irradiation should be developed as the next step of research.

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